

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-172078

(43)Date of publication of application : 26.06.2001

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(51)Int.Cl.

C04B 35/46  
H01L 41/09  
H01L 41/187

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(21)Application number : 2000-326638 (71)Applicant : MURATA MFG CO LTD

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### (54) PIEZOELECTRIC CERAMIC COMPOSITION AND PIEZOELECTRIC CERAMIC ELEMENT USING THE SAME

#### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a piezoelectric ceramic composition useful as a material for piezoelectric ceramic elements such as piezoelectric filter, piezoelectric vibrator and piezoelectric ceramic oscillator exhibiting ( $\geq 20\%$ ) electromechanical coupling factor  $k_t$  and ( $\leq 45$ ) temperature-changing rate  $frTC$  of resonance frequency which are practically usable by improving an electromechanical coupling factor  $k_t$  and a temperature-changing rate  $frTC$  of resonance frequency at  $-20^\circ\text{C}$  to  $80^\circ\text{C}$  of piezoelectric ceramic composition consisting essentially of  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  and a piezoelectric ceramic element using the above ceramic composition.

SOLUTION: This piezoelectric ceramic composition comprises a main component represented by the general formula  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ . In the composition, at least one kind of element of Sc and Y is contained in an amount of  $\leq 0.1$  mol and  $> 0$  based on 1 mol Bi in the main component represented by the above general formula.

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[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

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[Date of requesting appeal against  
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[Date of extinction of right]

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CLAIMS

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[Claim(s)]

[Claim 1] The piezoelectric-ceramics constituent characterized by carrying out 0.1-mol or less (0 not being included) content of at least one sort in Sc and Y to Bi in said principal component, and one mol in the piezoelectric-ceramics constituent which uses as a principal component the bismuth stratified compound which consists of Sr, Bi, Ti, and O at least.

[Claim 2] The piezoelectric-ceramics constituent characterized by carrying out 0.1-mol or less (0 not being included) content of at least one sort in Sc and Y to Bi in the principal component expressed with said general formula, and one mol in the piezoelectric-ceramics constituent which consists of a principal component expressed with general formula  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ .

[Claim 3] It is  $\text{Mn MnCO}_3$  Piezoelectric-ceramics constituent according to claim 1 or 2 characterized by converting and carrying out content 1.5 or less (0 not being included) % of the weight.

[Claim 4] The piezo-electric ceramic component containing the electrode formed in the piezoelectric ceramics which consist of a piezoelectric-ceramics constituent according to claim 1 to 3, and said piezoelectric ceramics.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the piezo-electric ceramic component using a piezoelectric-ceramics constituent and it useful as ingredients, such as piezo-electric ceramic components, such as a piezo-electric ceramic filter, a piezo-electric ceramic radiator, and a piezo-electric ceramic vibrator, especially about the piezo-electric ceramic component which used a piezoelectric-ceramics constituent and it, for example.

[0002]

[Description of the Prior Art] The piezoelectric-ceramics constituent which uses titanate-acid lead zirconate ( $\text{Pb}(\text{Ti}_x \text{Zr } 1-x) \text{O}_3$ ) or lead titanate ( $\text{PbTiO}_3$ ) as a principal component is conventionally used widely as a piezoelectric-ceramics constituent used for piezo-electric ceramic components, such as a piezo-electric ceramic filter, a piezo-electric ceramic radiator, and a piezo-electric ceramic vibrator. However, in the piezoelectric-ceramics constituent which uses titanate-acid lead zirconate or lead titanate as a principal component, since lead was contained so much during the presentation, there was a problem that the homogeneity of a product fell in a manufacture process for evaporation of a plumbic acid ghost. In order to prevent the homogeneous fall of the product by evaporation of the plumbic acid ghost in a manufacture process, or lead is not included at all during a presentation, the piezoelectric-ceramics constituent only containing small quantity is desirable. In the piezoelectric-ceramics [ this ] constituent which carry out a pair and use bismuth stratified compounds, such as  $\text{SrBi}_4 \text{Ti}_4 \text{O}_{15}$ , as a principal component, since a plumbic acid ghost is not contained during the presentation, the above problems are not produced.

[0003]

[Problem(s) to be Solved by the Invention] In the piezoelectric-ceramics constituent which uses  $\text{SrBi}_4 \text{Ti}_4 \text{O}_{15}$  etc. as a principal component, since the rate  $\text{frTC}$  of a temperature change with a resonance frequency of -20 to 80 degrees C [ an electromechanical coupling coefficient  $k_t$  indicates small below the titanate-acid lead zirconate or lead titanate used for piezo-electric ceramic components, such as a piezo-electric ceramic filter, a piezo-electric ceramic radiator, and a piezo-electric ceramic vibrator, from the former to be compared with the piezoelectric-ceramics constituent used as a principal component ] is large, practical use has come [ however, ] to be presented widely.

$\text{frTC} = (\text{fr}(\text{max}) - \text{fr}(\text{min})) / (\text{fr}(20 \text{ degrees C}), 100)$

$\text{fr}(\text{max})$ : Minimum resonance frequency  $\text{fr}(20 \text{ degrees C})$ : 20 degree C [ in the resonance frequency  $\text{fr}(\text{min})$ : -20 degree C to 80 degrees C No.1 temperature requirement in a -20 degree C to 80 degrees C temperature requirement ] resonance frequency [0004] So, the main purpose of this invention improves the rate  $\text{frTC}$  of a temperature change with an electromechanical coupling coefficient [ of the piezoelectric-ceramics constituent which uses  $\text{SrBi}_4 \text{Ti}_4 \text{O}_{15}$  as a principal component /  $k_t$  ], and a resonance frequency of -20 to 80 degrees C. The piezo-electric ceramic filter in which the rate  $\text{frTC}$  of a temperature change (45 or less) of the electromechanical coupling coefficient  $k_t$  (20% or more) of extent with which practical use can be presented, and resonance frequency is shown, It is offering the piezo-electric ceramic component using a piezoelectric-ceramics constituent and it useful as ingredients, such as piezo-electric ceramic components, such as a piezo-electric ceramic radiator and a piezo-electric ceramic vibrator.

[0005]

[Means for Solving the Problem] The piezoelectric-ceramics constituent concerning this invention is a piezoelectric-ceramics constituent characterized by carrying out 0.1-mol or less (0 not being included) content of at least one sort in Sc and Y to Bi in said principal component, and one mol in the piezoelectric-ceramics constituent which uses as a principal component the bismuth stratified compound which consists of Sr, Bi, Ti, and O at least. Moreover, the piezoelectric-ceramics constituent concerning this invention is a piezoelectric-ceramics constituent characterized by carrying out 0.1-mol or less (0 not being included) content of at least one sort in Sc and Y to Bi in the principal component expressed with that general formula, and one mol in the piezoelectric-ceramics constituent which consists of a principal component expressed with general formula  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ . With the piezoelectric-ceramics constituent concerning this invention, Mn is  $\text{MnCO}_3$ . Content may be converted and carried out 1.5 or less (0 is not included) % of the weight. The piezoelectric ceramic component concerning this invention is a piezo-electric ceramic component containing the piezoelectric ceramics which consist of a piezoelectric-ceramics constituent concerning this invention, and the electrode formed in piezoelectric ceramics. In addition, although the principal component in the piezoelectric-ceramics constituent concerning this invention is expressed with general formula  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ , the mole ratio of each element may have a gap of some.

[0006] In the piezoelectric-ceramics constituent concerning this invention, to Bi and one mol, when [ than this ] more, the fall of an electromechanical coupling coefficient  $k_t$  is seen, and the practical electromechanical coupling coefficient  $k_t$  is not obtained, or the content of Sc and Y was set to 0.1 mols or less (0 is not included), because the porcelain which can be polarized was not obtained. Moreover, although Takahashi and others shows clearly that an electromechanical coupling coefficient  $k_t$  improves by converting Mn into the piezoelectric-ceramics constituent which uses  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  as a principal component in Japanese Patent Application No. No. 85292 [ 48 to ] at MnO, and containing 0.005 to 0.7% of the weight Also in the piezoelectric-ceramics constituent which carried out optimum dose content of Mn, the effectiveness of the invention in this application is effective in the piezoelectric-ceramics constituent used as such a piezoelectric-ceramics constituent, i.e., a principal component, and a useful piezoelectric-ceramics constituent with the small rate  $\text{frTC}$  of a temperature change of resonance frequency with a still larger and electromechanical coupling coefficient  $k_t$  is obtained. It sets to invention concerning claim 3, and is the content of Mn  $\text{MnCO}_3$  When [ than this ] more, it converted and because the porcelain which can be polarized was not obtained, could be 1.5 or less (0 is not included) % of the weight. Moreover, since the rate  $\text{frTC}$  of a temperature change of resonance frequency becomes small especially in addition to improvement in an electromechanical coupling coefficient  $k_t$  when Y is chosen among the content elements of Sc and Y, the still more useful piezoelectric-ceramics constituent as ingredients, such as piezo-electric ceramic components, such as a piezo-electric ceramic filter, a piezo-electric ceramic radiator, and a piezo-electric ceramic vibrator, is obtained especially, for example.

[0007] The above-mentioned purpose of this invention, the other purposes, the description, and an advantage will become still clearer from detailed explanation of the gestalt of implementation of the following invention performed with reference to a drawing.

[0008]

[Embodiment of the Invention] (Example) First, as a start raw material,  $\text{SrCO}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Sc}_2\text{O}_3$ , and  $\text{Y}_2\text{O}_3$  are prepared, and it is presentation  $(\text{Sr}_{1-x}\text{M}_x)\text{Bi}_4\text{Ti}_4\text{O}_{15} + y$  % of the weight  $\text{MnCO}_3$  (M is either Sc and Y.) about these. And  $\text{MnCO}_3$   $0 \leq x \leq 0.45$ ,  $0 \leq y \leq 1.6$ . It \*\*\*\*(ed) so that it might become, and wet blending was carried out for about 4 hours using the ball mill, and mixture was obtained. After drying the obtained mixture, temporary quenching was carried out at 700-900 degrees C, and the temporary-quenching object was obtained. And after carrying out coarse grinding of this temporary-quenching object, wet grinding of the organic binder was carried out for 4 hours using optimum dose, in addition a ball mill, and grain refining was performed through the screen of 40 meshes. Next, it is this 1000kg/cm<sup>2</sup> Disc-like porcelain was obtained by casting by the pressure to a disk with a diameter [ of 12.5mm ], and a thickness of 2mm, and calcinating this at 1150-1250 degrees C in atmospheric air. After having applied the silver paste to the front face (both principal planes) of this porcelain by the usual approach, baking on it and forming a silver electrode

in it, the direct current voltage of 5-10kV/mm was impressed for 10 - 30 minutes in 150-200-degree C insulating oil, polarization processing was performed, and piezoelectric ceramics (sample) were obtained. And the rate frTC of a temperature change of an electromechanical coupling coefficient kt and resonance frequency was measured about the obtained sample. The result is shown in Table 1. In addition, it is indicated in Table 1 also as the symbol of element of M in the presentation of each sample, and the numeric value of x and y. Note that it is equivalent to the content (mol) of M to Bi and one mol,  $1/4$ ,  $x/4$  [ i.e., ], in the above-mentioned empirical formula of x, in Table 1.

[0009]

[Table 1]

試料 No	M	x	y (wt%)	kt (%)	frTC (ppm/°C)
1*	—	0	0	12	80
2	Y	0.1	0	24	35
3	Y	0.4	0	24	29
4*	Y	0.45	0	分極不可	—
5	Y	0.4	1.5	21	25
6*	Y	0.45	1.5	分極不可	—
7*	Y	0.4	1.6	分極不可	—
8	Sc	0.1	1	21	45
9	Sc	0.4	1	24	40
10*	Sc	0.45	1	分極不可	—

Sample \* mark of the No. column shows that this invention of that sample is out of range.

[0010] Since electromechanical coupling coefficients kt are in 20% or more and practical use level and the rate frTC of a temperature change of resonance frequency is all in 45 or less and practical use level about each sample concerning the example of this invention as shown in Table 1, it is especially clear that it is a piezoelectric-ceramics constituent useful as ingredients, such as piezoelectric ceramic components, such as a piezo-electric ceramic filter, a piezo-electric ceramic radiator, and a piezo-electric ceramic vibrator, for example. Moreover, in sample No.2 of the example of this invention, and 3 and 5, as shown in Table 1, when Y is included, it is clear that useful piezoelectric ceramics with the especially small rate frTC of a temperature change of resonance frequency are obtained.

[0011] In addition, the piezoelectric-ceramics constituent concerning this invention is not limited to the presentation of the above-mentioned example, and if it is within the limits of the summary of invention, it is effective.

[0012] Moreover, although the rate frTC of a temperature change of an electromechanical coupling coefficient kt and resonance frequency showed the example about the thickness longitudinal oscillation of a disc-like piezo-electric ceramic vibrator in the above-mentioned example The effectiveness of the invention in this application is not limited to the thickness longitudinal oscillation of a disc-like piezo-electric ceramic vibrator. The higher harmonic of thickness skid vibration or thickness longitudinal oscillation etc. is effective like the case of thickness longitudinal oscillation also in other oscillation modes especially used for a piezo-electric ceramic filter, a piezo-electric ceramic radiator, etc. as other piezo-electric ceramic components, for example.

[0013] Drawing 1 is the perspective view showing an example of the piezo-electric ceramic vibrator concerning this invention, and drawing 2 is that sectional view solution Fig. The piezo-electric ceramic vibrator 10 shown in drawing 1 and drawing 2 contains the rectangular parallelepiped-like piezoelectric ceramics 12. Piezoelectric ceramics 12 contain the piezoelectric-ceramics layers 12a and 12b of two sheets. These piezoelectric-ceramics layers 12a and 12b consist of a piezoelectric-ceramics constituent concerning this above-mentioned invention, and the laminating of them is carried out and they are formed in one. Moreover, as the arrow head of drawing 2 shows, polarization of these piezoelectric-ceramics layers 12a and 12b is carried out in the same thickness direction.

[0014] Among the piezoelectric-ceramics layers 12a and 12b, circular vibrating electrode 14a is

formed in the center, for example, and drawer electrode 16a of T typeface is formed covering the end side of piezoelectric ceramics 12 from vibrating electrode 14a. Moreover, circular vibrating electrode 14b is formed in the center, for example, and drawer electrode 16b of T typeface is formed in the front face of piezoelectric-ceramics layer 12a covering the other end side of piezoelectric ceramics 12 from vibrating electrode 14b. Furthermore, circular vibrating electrode 14c is formed in the center, for example, and drawer electrode 16c of T typeface is formed in the front face of piezoelectric-ceramics layer 12b covering the other end side of piezoelectric ceramics 12 from vibrating electrode 14c.

[0015] And one external terminal 20a is connected to drawer electrode 16a through lead-wire 18a, and external terminal 20b of another side is connected to the drawer electrodes 16b and 16c through another lead-wire 18b.

[0016] In addition, this invention is applied to other piezo-electric ceramic components, such as piezo-electric ceramic vibrators other than above-mentioned piezo-electric ceramic vibrator 10, a piezo-electric ceramic filter, and a piezo-electric ceramic radiator.

[0017]

[Effect of the Invention] According to this invention, it is the piezoelectric-ceramics constituent which uses  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  as a principal component, and an electromechanical coupling coefficient  $k_t$  is improved to 20% or more, and the rate of a temperature change of resonance frequency is improved by 45 or less, and the piezo-electric ceramic component using a piezoelectric-ceramics constituent and it useful as ingredients, such as piezo-electric ceramic components, such as a piezo-electric ceramic filter, a piezo-electric ceramic radiator, and a piezo-electric ceramic vibrator, is obtained especially, for example.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the perspective view showing an example of the piezo-electric ceramic vibrator concerning this invention.

[Drawing 2] It is the sectional view solution Fig. of the piezo-electric ceramic vibrator shown in drawing 1 .

[Description of Notations]

10 Piezo-electric Ceramic Vibrator

12 Piezoelectric Ceramics

12a, 12b Piezoelectric-ceramics layer

14a, 14b, 14c Vibrating electrode

16a, 16b, 16c Drawer electrode

18a, 18b Lead wire

20a, 20b External terminal

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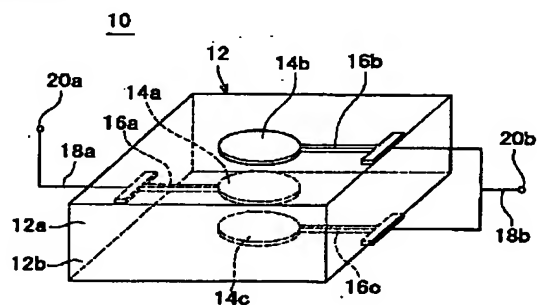
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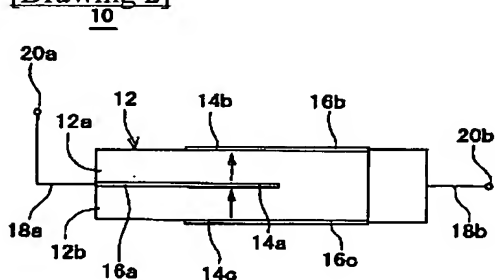
DRAWINGS

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[Drawing 1]



[Drawing 2]



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(54) PIEZOELECTRIC CERAMIC COMPOSITION AND PIEZOELECTRIC CERAMIC ELEMENT USING THE SAME

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PROBLEM TO BE SOLVED: To provide a piezoelectric ceramic composition useful as a material for piezoelectric ceramic elements such as piezoelectric filter, piezoelectric vibrator and piezoelectric ceramic oscillator exhibiting ( $\geq 20\%$ ) electromechanical coupling factor  $k_t$  and ( $\leq 45$ ) temperature-changing rate  $frTC$  of resonance frequency which are practically usable by improving an electromechanical coupling factor  $k_t$  and a temperature-changing rate  $frTC$  of resonance frequency at  $-20^\circ\text{C}$  to  $80^\circ\text{C}$  of piezoelectric ceramic composition consisting essentially of  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  and a piezoelectric ceramic element using the above ceramic composition.

SOLUTION: This piezoelectric ceramic composition comprises a main component represented by the general formula  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ . In the composition, at least one kind of element of Sc and Y is contained in an amount of  $\leq 0.1$  mol and  $>0$  based on 1 mol Bi in the main component represented by the above general formula.

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[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

(19)日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11)特許出願公開番号  
特開2001-172078  
(P2001-172078A)

(43)公開日 平成13年6月26日(2001.6.26)

(51)Int.Cl. <sup>7</sup>	識別記号	F I	テ-マコ-ト(参考)
C 0 4 B 35/46		C 0 4 B 35/46	J
H 0 1 L 41/09		H 0 1 L 41/08	C
41/187		41/18	1 0 1 J

審査請求 未請求 請求項の数4 O L (全 4 頁)

(21)出願番号 特願2000-326638(P2000-326638)  
(62)分割の表示 特願平11-308786の分割  
(22)出願日 平成11年10月29日(1999.10.29)

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(54)【発明の名称】 圧電磁器組成物およびそれを用いた圧電セラミック素子

(57)【要約】

【課題】  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  を主成分とする圧電磁器組成物の電気機械結合係数  $k_t$  および  $-20^\circ\text{C}$  から  $80^\circ\text{C}$  の共振周波数の温度変化率  $f_r\text{TC}$  を改善し、実用に供しうる程度の電気機械結合係数  $k_t$  (20%以上) および共振周波数の温度変化率  $f_r\text{TC}$  (45以下) を示す圧電セラミックフィルタ、圧電セラミック発振子および圧電セラミック振動子などの圧電セラミック素子などの材料として有用な圧電磁器組成物およびそれを用いた圧電セラミック素子を提供する。

【解決手段】 圧電磁器組成物は、一般式  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  で表される主成分からなる圧電磁器組成物において、Sc および Y のうちの少なくとも1種をその一般式で表される主成分中の Bi、1mol に対して 0.1mol 以下 (0 を含まない) 含有することを特徴とする。

## 【特許請求の範囲】

【請求項1】 少なくとも  $Sr$ 、 $Bi$ 、 $Ti$ 、 $O$  からなるピスマス層状化合物を主成分とする圧電磁器組成物において、 $Sc$  および  $Y$  のうちの少なくとも1種を前記主成分中の  $Bi$ 、 $1mol$  に対して  $0.1mol$  以下 ( $0$  を含まない) 含有することを特徴とする、圧電磁器組成物。

【請求項2】 一般式  $SrBi_4Ti_4O_{15}$  で表される主成分からなる圧電磁器組成物において、 $Sc$  および  $Y$  のうちの少なくとも1種を前記一般式で表される主成分中の  $Bi$ 、 $1mol$  に対して  $0.1mol$  以下 ( $0$  を含まない) 含有することを特徴とする、圧電磁器組成物。

【請求項3】  $Mn$  を  $MnCO_3$  に換算して  $1.5$  重量%以下 ( $0$  を含まない) 含有することを特徴とする、請求項1または請求項2に記載の圧電磁器組成物。

【請求項4】 請求項1ないし請求項3のいずれかに記載の圧電磁器組成物からなる圧電磁器、および前記圧電磁器に形成される電極を含む、圧電セラミック素子。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 この発明は圧電磁器組成物およびそれをを用いた圧電セラミック素子に関し、特にたとえば、圧電セラミックフィルタ、圧電セラミック発振子および圧電セラミック振動子などの圧電セラミック素子などの材料として有用な圧電磁器組成物およびそれをを用いた圧電セラミック素子に関する。

## 【0002】

【従来の技術】 圧電セラミックフィルタ、圧電セラミック発振子および圧電セラミック振動子などの圧電セラミック素子に用いられる圧電磁器組成物として、従来、チタン酸ジルコン酸鉛 ( $Pb(Ti, Zr)O_3$ ) またはチタン酸鉛 ( $PbTiO_3$ ) を主成分とする圧電磁器組成物が広く用いられている。しかしながら、チタン酸ジルコン酸鉛またはチタン酸鉛を主成分とする圧電磁器組成物では、その組成中に鉛を多量に含有するため、製造過程において鉛酸化物の蒸発のため製品の均一性が低下するという問題があった。製造過程における鉛酸化物の蒸発による製品の均一性の低下を防止するためには、組成中に鉛をまったく含まないまたは少量のみ含む圧電磁器組成物が好ましい。これに対して、 $SrBi_4Ti_4O_{15}$  などのピスマス層状化合物を主成分とする圧電磁器組成物では、その組成中に鉛酸化物を含有しないため、上記のような問題は生じない。

## 【0003】

【発明が解決しようとする課題】 しかしながら、 $SrBi_4Ti_4O_{15}$  などを主成分とする圧電磁器組成物では、従来から圧電セラミックフィルタ、圧電セラミック発振子および圧電セラミック振動子などの圧電セラミック素子に用いられているチタン酸ジルコン酸鉛またはチタン酸鉛を主成分とする圧電磁器組成物に比べて、電気

機械結合係数  $k_t$  が小さくかつ以下に示す  $-20^\circ C$  から  $80^\circ C$  の共振周波数の温度変化率  $f_rTC$  が大きいため、広く実用に供されるに至っていない。

$$f_rTC = (f_r(\max) - f_r(\min)) / (f_r(20^\circ C) \cdot 100)$$

$f_r(\max)$  :  $-20^\circ C$  から  $80^\circ C$  の温度範囲において最高の共振周波数

$f_r(\min)$  :  $-20^\circ C$  から  $80^\circ C$  の温度範囲において最低の共振周波数

$f_r(20^\circ C)$  :  $20^\circ C$  での共振周波数

【0004】 それゆえに、この発明の主たる目的は、 $SrBi_4Ti_4O_{15}$  を主成分とする圧電磁器組成物の電気機械結合係数  $k_t$  および  $-20^\circ C$  から  $80^\circ C$  の共振周波数の温度変化率  $f_rTC$  を改善し、実用に供しうる程度の電気機械結合係数  $k_t$  ( $20\%$  以上) および共振周波数の温度変化率  $f_rTC$  ( $45$  以下) を示す圧電セラミックフィルタ、圧電セラミック発振子および圧電セラミック振動子などの圧電セラミック素子などの材料として有用な圧電磁器組成物およびそれをを用いた圧電セラミック素子を提供することである。

## 【0005】

【課題を解決するための手段】 この発明にかかる圧電磁器組成物は、少なくとも  $Sr$ 、 $Bi$ 、 $Ti$ 、 $O$  からなるピスマス層状化合物を主成分とする圧電磁器組成物において、 $Sc$  および  $Y$  のうちの少なくとも1種を前記主成分中の  $Bi$ 、 $1mol$  に対して  $0.1mol$  以下 ( $0$  を含まない) 含有することを特徴とする、圧電磁器組成物である。また、この発明にかかる圧電磁器組成物は、一般式  $SrBi_4Ti_4O_{15}$  で表される主成分からなる圧電磁器組成物において、 $Sc$  および  $Y$  のうちの少なくとも1種をその一般式で表される主成分中の  $Bi$ 、 $1mol$  に対して  $0.1mol$  以下 ( $0$  を含まない) 含有することを特徴とする、圧電磁器組成物である。この発明にかかる圧電磁器組成物では、 $Mn$  が  $MnCO_3$  に換算して  $1.5$  重量%以下 ( $0$  を含まない) 含有されてもよい。この発明にかかる圧電セラミック素子は、この発明にかかる圧電磁器組成物からなる圧電磁器と、圧電磁器に形成される電極とを含む、圧電セラミック素子である。なお、この発明にかかる圧電磁器組成物における主成分は一般式  $SrBi_4Ti_4O_{15}$  で表されるが、それぞれの元素のモル比は多少のずれがあってもかまわない。

【0006】 この発明にかかる圧電磁器組成物において、 $Sc$  および  $Y$  の含有量を  $Bi$ 、 $1mol$  に対して  $0.1mol$  以下 ( $0$  を含まない) としたのは、これより多い場合には、電気機械結合係数  $k_t$  の低下がみられ、実用的な電気機械結合係数  $k_t$  が得られない、または、分極可能な磁器が得られないためである。また、高橋らは、特願昭 48-85292 号において、 $SrBi_4Ti_4O_{15}$  を主成分とする圧電磁器組成物に  $Mn$  を  $M$

nOに換算して0.005~0.7重量%含有することにより、電気機械結合係数 $k_t$ が向上することを明らかにしているが、このような圧電磁器組成物すなわち主成分となる圧電磁器組成物にMnを適量含有した圧電磁器組成物においても、本願発明の効果は有効であり、電気機械結合係数 $k_t$ がさらに大きくかつ共振周波数の温度変化率 $f_r T C$ が小さい有用な圧電磁器組成物が得られる。請求項3にかかる発明において、Mnの含有量をMnCO<sub>3</sub>に換算して1.5重量%以下(0を含まない)としたのは、これより多い場合には分極可能な磁器が得られないためである。また、ScおよびYの含有元素のうちYを選択した場合には、電気機械結合係数 $k_t$ の向上に加え、共振周波数の温度変化率 $f_r T C$ が特に小さくなるため、特にたとえば、圧電セラミックフィルタ、圧電セラミック発振子および圧電セラミック振動子などの圧電セラミック素子などの材料としてさらに有用な圧電磁器組成物が得られる。

【0007】この発明の上述の目的、その他の目的、特徴および利点は、図面を参照して行う以下の発明の実施の形態の詳細な説明から一層明らかとなろう。

【0008】

【発明の実施の形態】(実施例) まず、出発原料として、SrCO<sub>3</sub>、Bi<sub>2</sub>O<sub>3</sub>、TiO<sub>2</sub>、Sc<sub>2</sub>O<sub>3</sub>、Y<sub>2</sub>O<sub>3</sub>およびMnCO<sub>3</sub>を用意し、これらを組成(Sr<sub>1-x</sub>M<sub>x</sub>)Bi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>+y重量%MnCO<sub>3</sub> \*

試料 No.	M	x	y (wt%)	$k_t$ (%)	$f_r T C$ (ppm/°C)
1*	—	0	0	12	80
2	Y	0.1	0	24	35
3	Y	0.4	0	24	29
4*	Y	0.45	0	分極不可	—
5	Y	0.4	1.5	21	25
6*	Y	0.45	1.5	分極不可	—
7*	Y	0.4	1.8	分極不可	—
8	Sc	0.1	1	21	45
9	Sc	0.4	1	24	40
10*	Sc	0.45	1	分極不可	—

試料 No. 欄の\*印はその試料がこの発明の範囲外であることを示す。

【0010】表1に示すように、この発明の実施例にかかる各試料については、いずれも、電気機械結合係数 $k_t$ が20%以上と実用レベルにありかつ共振周波数の温度変化率 $f_r T C$ が45以下と実用レベルにあることから、特にたとえば、圧電セラミックフィルタ、圧電セラミック発振子および圧電セラミック振動子などの圧電セラミック素子などの材料として有用な圧電磁器組成物であることが明らかである。また、表1に示すように、Yを含む場合、すなわち、この発明の実施例の試料No. 2、3および5においては、共振周波数の温度変化率 $f$

\*、(Mは、ScおよびYのいずれか。 $0 \leq x \leq 0.45$ 、 $0 \leq y \leq 1.6$ 。)となるように秤取して、ボールミルを用いて約4時間湿式混合して、混合物を得た。得られた混合物を乾燥した後、700~900℃で仮焼して、仮焼物を得た。それから、この仮焼物を粗粉碎した後、有機バインダを適量加えてボールミルを用いて4時間湿式粉碎し、40メッシュのふるいを通して粒度調整を行った。次に、これを1000kg/cm<sup>2</sup>の圧力で直径12.5mm、厚さ2mmの円板に成型し、これを大気中で1150~1250℃で焼成することによって、円板状の磁器を得た。この磁器の表面(両主面)に、通常の方法により銀ペーストを塗布し焼付けて銀電極を形成した後、150~200℃の絶縁オイル中で5~10kV/mmの直流電圧を10~30分間印加して分極処理を施し、圧電磁器(試料)を得た。そして、得られた試料について、電気機械結合係数 $k_t$ および共振周波数の温度変化率 $f_r T C$ を測定した。その結果を表1に示す。なお、表1には、各試料の組成におけるMの元素記号と、xおよびyの数値とも示す。表1において、上記の組成式中のxの1/4すなわちx/4がBi、1molに対してのMの含有量(mol)に相当することに注意されたい。

【0009】

【表1】

$f_r T C$ が特に小さい有用な圧電磁器が得られることが明らかである。

【0011】なお、この発明にかかる圧電磁器組成物は上記の実施例の組成に限定されるものではなく、発明の要旨の範囲内であれば有効である。

【0012】また、上述の実施例では電気機械結合係数 $k_t$ および共振周波数の温度変化率 $f_r T C$ は円板状の圧電セラミック振動子の厚み縦振動についての例を示したが、本願発明の効果は、円板状の圧電セラミック振動子の厚み縦振動に限定されず、厚みすべり振動や厚み縦振動の高調波など、他の圧電セラミック素子として特にたとえば圧電セラミックフィルタや圧電セラミック発振

子などに利用される他の振動モードにおいても、厚み縦振動の場合と同様に有効である。

【0013】図1はこの発明にかかる圧電セラミック振動子の一例を示す斜視図であり、図2はその断面図解図である。図1および図2に示す圧電セラミック振動子10は、たとえば直方体状の圧電磁器12を含む。圧電磁器12は、2枚の圧電磁器層12aおよび12bを含む。これらの圧電磁器層12aおよび12bは、上述のこの発明にかかる圧電磁器組成物からなり、積層されかつ一体的に形成される。また、これらの圧電磁器層12aおよび12bは、図2の矢印で示すように、同じ厚み方向に分極されている。

【0014】圧電磁器層12aおよび12bの間には、その中央にたとえば円形の振動電極14aが形成され、その振動電極14aから圧電磁器12の一端面にわたってたとえばT字形の引出電極16aが形成される。また、圧電磁器層12aの表面には、その中央にたとえば円形の振動電極14bが形成され、その振動電極14bから圧電磁器12の他端面にわたってたとえばT字形の引出電極16bが形成される。さらに、圧電磁器層12bの表面には、その中央にたとえば円形の振動電極14cが形成され、その振動電極14cから圧電磁器12の他端面にわたってたとえばT字形の引出電極16cが形成される。

【0015】そして、引出電極16aにはリード線18aを介して一方の外部端子20aが接続され、引出電極16bおよび16cには別のリード線18bを介して他\*

\*方の外部端子20bが接続される。

【0016】なお、この発明は、上述の圧電セラミック振動子10以外の圧電セラミック振動子、圧電セラミックフィルタおよび圧電セラミック発振子などの他の圧電セラミック素子にも適用される。

【0017】

【発明の効果】この発明によれば、 $\text{SrBi}_4\text{Ti}_2\text{O}_{15}$ を主成分とする圧電磁器組成物であって、電気機械結合係数 $k_t$ が20%以上に改善されかつ共振周波数の温度変化率が45以下に改善され、特にたとえば圧電セラミックフィルタ、圧電セラミック発振子および圧電セラミック振動子などの圧電セラミック素子などの材料として有用な圧電磁器組成物およびそれを用いた圧電セラミック素子が得られる。

【図面の簡単な説明】

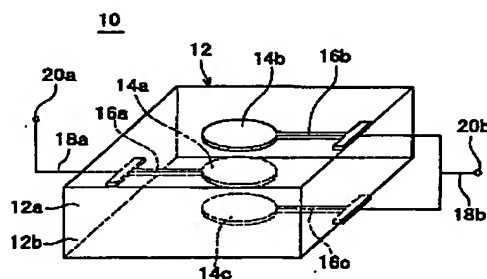
【図1】この発明にかかる圧電セラミック振動子の一例を示す斜視図である。

【図2】図1に示す圧電セラミック振動子の断面図解図である。

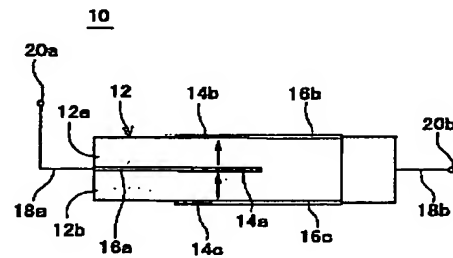
【符号の説明】

- 10 圧電セラミック振動子
- 12 圧電磁器
- 12a、12b 圧電磁器層
- 14a、14b、14c 振動電極
- 16a、16b、16c 引出電極
- 18a、18b リード線
- 20a、20b 外部端子

【図1】



【図2】



フロントページの続き

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